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Compatibilization of poly(methyl acrylate) and polysterene through charge transfer interactions

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Summary

Two incompatible copolymers, poly(methyl acrylate) and polystyrene have been compatibilized through charge transfer interactions. Methyl acrylate was copolymerized with an electron donor and styrene was copolymerized with an electron acceptor. Interaction between the electron donor, N-vinylcarbazole, and the electron acceptor, 2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate was sufficiently strong to overcome the reluctance to mix when interactive group concentrations were above 12 mole%.

Introduction

In the search for polymers with new properties, there is a continual effort to employ familiar polymers in new combinations. Blends of polymers may result in a new polymer mixture with desirable properties contributed by each of the components. When polymers are blended they rarely form a compatible mixture. Compatibility may be defined as the presence of a single phase. One method of inducing compatibilization is to include a small number of interactive groups, enough to provide a sufficiently strong interaction to overcome the repulsive forces between the two incompatible polymers. Among the interactive pairs that can provide the necessary negative heat of mixing (1) are electron acceptors and electron donors.

Several groups have attempted compatibilization of polymers through charge transfer interactions. The interaction between the electron donor and the electron acceptor can be strong enough to result in a compatible mixture or an improvement in properties unaccompanied by compatibilization. Donor and acceptor groups have been incorporated by copolymerization with an acrylate with pendant interactive groups or by post-polymerization modification. Post-polymerization on both copolymers and homopolymers has been employed. Schneider *et al.* (2) found that viscoelastic behavior in incompatible blends of poly(butyl methacrylate) with poly(methyl methacrylate) or polydimethylsiloxane was improved by charge-transfer interactions. Butyl methacrylate was copolymerized with either an acceptor, 2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate (**DNBM**), or a donor, 2-(9-carbazolyl)ethyl methacrylate (**HECM**)). Acceptor modified poly(butyl methacrylate) was blended with the donor copolymer

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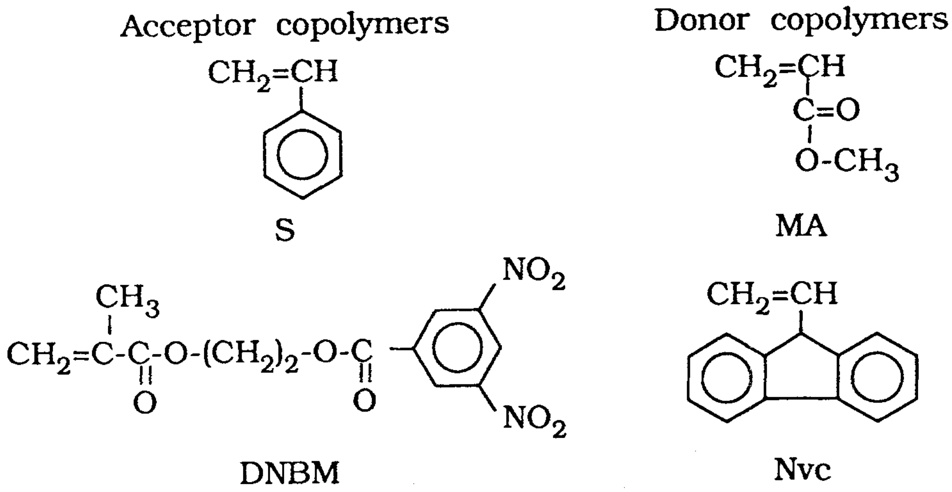
*To whom offprint requests should be sent poly(methyl methacrylate-co-HECM). Incorporation of an acceptor group into polydimethylsiloxane was achieved indirectly through post-polymerization modification of the copolymer poly(dimethylsiloxane-co-hydrogen methylsiloxane). The resultant poly(dimethylsiloxane-co-4-((3,5-dinitrobenzoyl)oxy)butyl methylsiloxane) was blended with the donor modified poly(butyl methacrylate). Pugh and Percec (3) compatibilized poly(2,6-dimethylphenylene oxide) and polyepichlorohydrin by post polymerization modification of the polymers. Acceptor 3,5-dinitrobenzoyl groups on poly(2,6-dimethylphenylene oxide) and various donor carbazole groups on and polyepichlorohydrin provided the necessary interaction. Epple and Schneider (4) achieved compatibility between methyl acrylate and n-butyl acrylate by copolymerization with an electron donor and an electron acceptor. Whether the donor, 2-((N-carbazolyl)oxy) ethyl acrylate was copolymerized with n-butyl acrylate or with methyl acrylate, the interaction of the donor with the acceptor 2-((3,5-dinitrobenzoyl)oxy) ethyl acrylate was strong enough to overcome the reluctance to mix. Schneider *et. al.* (5) performed post polymerization modifications on poly(dimethylsiloxane-co-hydrogen methylsiloxane) and poly(cellulose tripropionate) to include electron acceptors and donors in an attempt to compatibilize polydimethylsiloxane and poly(cellulose tripropionate). The electron acceptor group was 3,5-dinitrobenzoate and the donor group was N-propylcarbazole. Though compatibility was not achieved, the modified polymer blends exhibited better rheological properties than the unmodified polymer blends.

The aim of compatibilization is to derive a new polymer with properties based upon those of the parent polymers. Significant concentrations of the interactive groups would result in alteration of the properties of the parent polymers and a more complex system, hence a system requiring a low concentration of interactive groups is sought. Schneider *et al.* restricted the concentration of interactive groups in blended copolymers of poly(butyl methacrylate), poly(methyl methacrylate) and polydimethylsiloxane to 10% or less. This concentration was not sufficient to compatibilize the system. Pugh and Percec achieved compatibilization of poly(2,6-dimethylphenylene oxide) and polyepichlorohydrin with 25% interactive groups. The butyl acrylate and methyl acrylate system studied by Epple and Schneider requires concentrations of interactive groups exceeding 35% to compatibilize the polymers.

The incompatible polymers chosen for this study are polystyrene and poly(methyl acrylate). Electron donor and acceptor groups are introduced in the system through free radical copolymerization. Styrene (**S**) is copolymerized with the acceptor, 2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate (**DNBM**) and the second component, methyl acrylate (**MA**), is copolymerized with the donor, N-vinylcarbazole (**Nvc**). Structures of the monomers are depicted in Scheme 1. Compatibility is determined by glass transition behavior of the blends.

Modeling of glass transitions of multi-component systems has been attempted with several equations which assign weights

Scheme 1



to the Tg's of the components. Four of these include terms dependent on the distribution of sequences in copolymers. The Barton (6), Johnston (7) and Couchman (8) equations include diad terms and the Ham (9) equation includes triad distributions. Interactions in copolymers are generally weak consequently the equations describing Tg are linear, first-order equations. The stronger interactions used to compatibilize polymer blends are modeled with higher order or non-linear equations, such as the Breckner (10) and Kwei (11) equations. These equations also apply to copolymers with strong interactions between the components.

Experimental

Acceptor copolymers

The monomer DNBM was synthesized from 3,5-dinitrobenzoic acid, ethylene glycol and methacryloyl chloride according to published methods (12). Free radical copolymerization of S and DNBM was carried out in toluene with AIBN as initiator. Polymerization solutions with monomer concentrations of 1.5M and initiator at 1% of the monomer weight were purged with nitrogen, sealed in glass ampoules and maintained at 60° for three days. Polymers were isolated by precipitation into methanol followed by reprecipitation from tetrahydrofuran into methanol. Since monomer conversions were very low, polymerizations were carried out in the presence of an inert electron donor, N-ethyl carbazole in the hope that conversions would increase. A similar electron-accepting monomer has been found to homopolymerize only in the presence of an inert electron donor (13). The increase in conversion of the poly(S-co-DNBM) copolymers was negligible, nonetheless, polymerizations were continued in the presence of the electron donor. Batch sizes and initiator concentration were increased to provide sufficient quantities for blending. The resultant

Table 1 Polymerization details of poly(S-co-DNBM) synthesis

Copolymer	Monomer Feed Composition (mole% DNBM)	Monomer Conversion (wt %)	Copolymer Composition (mole% DNBM)
copA1	5.8	3.6	7.2
copA2	9.4	2.8	13
copA3	13	3.9	17
copA4	14	3.0	21
copA5	24	4.5	30

copolymers are referred to as acceptor copolymers (**copA**). Monomer feed compositions, monomer conversions and copolymer compositions are listed in Table 1.

Donor copolymers

Synthesis of poly(MA-co-Nvc) copolymers is described in another paper (14). These copolymers containing the donor group are referred to as donor copolymers (**copD**).

Blends

Polymers were dissolved separately in warm THF prior to blending. After slow evaporation of the solvent, the blends were dried under vacuum for four days at 80°C. Compositions of blend components are presented in Table 2.

Thermal analysis of the homopolymers, copolymers and blends was done by a Mettler differential scanning calorimeter (DSC) with a TC10A processor. The heating rate was 20°per minute, reported Tg's are from the second scan. Copolymers were analyzed on a Waters Associates gel permeation chromatograph (GPC) equipped with μStyragel columns to determine their number average molecular weights, $\overline{M}_n$. A flow rate of 1.0mL per minute was used, and samples were dissolved in THF at a concentration of 0.2wt %. Molecular weights were determined from a universal calibration curve.

Results and Discussion

Copolymer molecular weights reveal that the acceptor copolymers are very much shorter than the donor copolymers. Molecular weights, $\overline{M}_n$, of the acceptor copolymers ranged from 2,800 to 3,300 g/mol. These molecular weights correspond to degrees of polymerization between 18 and 26. It can be assumed that the chains of the acceptor copolymers are short with a maximum of three interactive groups each. On the other hand the donor copolymers have molecular weights between 19,000 and 72,000. Therefore the donor copolymer chains are long with at least 16 interactive groups on each chain.

Six series of blends were prepared from the donor and acceptor copolymers with comparable concentrations of interactive groups as described in Table 2. In each series there is a blend in which R, the ratio of donor to acceptor groups is equal to 1. Blends of the pale yellow acceptor

Table 2 Blended copolymers

Blend Series	Acceptor Copolymer		Donor Copolymer	
	Copolymer	Composition (mole% DNBM)	Copolymer	Composition (mole% Nvc)
B1	copA1	7.2	copD1	8.3
B2	copA2	13	copD2	11
B3	copA3	17	copD2	11
B4	copA3	17	copD3	12
B5	copA4	21	copD4	24
B6	copA5	30	copD5	33

copolymers and the white donor copolymers are orange. The change in color indicates charge transfer interaction. Glass transition temperatures of the blends in each series are plotted against the weight fraction of donor copolymer in Figure 1. Blends of copD1 and copA1 constituting series B1 appear cloudy and are in fact phase separated as indicated by the DSC results. Blends in the B1 series of Figure 1 exhibit two Tg's. The lower Tg is the same as the Tg of copD1, the higher Tg is lower than that of copA1. The Tg's are 35°apart and are essentially unchanged in each of the B1 blends. Depression of Tg is associated with an increase in free volume or a decrease in packing efficiency (15). The higher of the two Tg's may be due to a copA1 phase constrained to a more inefficient packing than pure copA1. Pinning of one end or the center of a short copA1 chain could force the copA1 chain to straighten out and protrude from the copD1 surface. Conceivably, the long copD1 chains would be better able to fold among one another, packing as in pure copD1. Since the Tg's of the blends with R<1 are the same as in the blends with R>1, it seems that packing in the copA1 phase is similar in the disperse and continuous phases.

The situation in series B2 of Figure 1 is more complex. Blends with R<1 have two Tg's and blends with R>1 have one Tg. The increased interactive group concentration from series B1 to series B2 results in some compatibilization. In the phase separated blends the upper Tg is just below the weighted average line and the lower Tg is slightly below that of the pure copD2 copolymer. The high Tg's of the phase separated blends and the Tg's of the compatible blends follow a reasonably smooth curve below the weighted average line. We believe that the upper Tg is due to a compatibilized phase in the presence of an incompatible excess of copD. Measurement of the changes in heat capacity, ΔCp, indicates that most of the polymer is in the compatibilized phase. The ΔCp values of the lower transitions in the phase separated blends are less than 10% of the total ΔCp. The presence of two phases at low copD content appears to be a function of the charge transfer interaction between the dinitrobenzoyl group and the carbazole group. Simmons and Natansohn (16) have observed a similar phase separation in blends of poly(DNBM) and a donor homopolymer containing 3-substituted carbazole groups. The

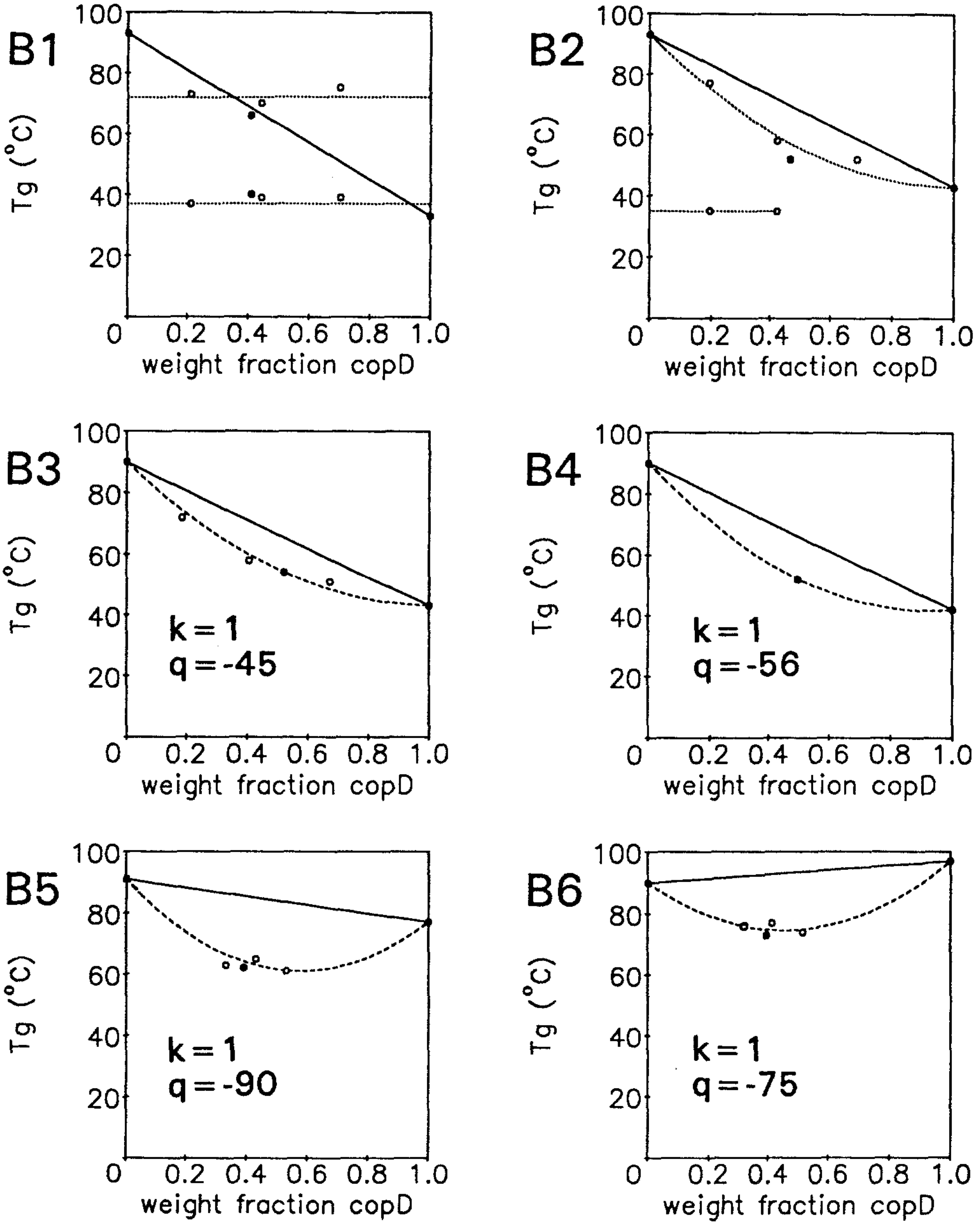


Figure 1 Glass transition temperatures of copolymers and blends in the six blend series; ∘ experimental data, • R=1; ——— weighted average of copolymers, ——— approximate fit, -------- best fit with Kwei's equation; k and q are fitting parameters of Kwei's equation

blends are compatible when the donor homopolymer content exceeds 35 mole%.

In series B3 through B6 of Figure 1, there is one Tg per blend and hence one phase. The modified polymers are compatible. The blend Tg's are below the mean Tg of the copolymers in each of the series. A fit of the data was made in order to investigate the relationship between the extent of depression and the concentration of interactive groups. Of the equations suitable for for analysis of blends with specific interactions, the Kwei equation (15) was chosen. The constants k and q are the fitting parameters, w is the weight fraction of polymer 1, Tg_1 and Tg_2 are the Tg's of the component polymers.

$$Tg = \frac{Tg_1 + w(kTg_2 - Tg_1)}{1 + w(k-1)} + q(w-w^2)$$

When k=1 and q is negative, the curve shows no inflection point and lies below the weighted average of the component Tg's. The values of q and k, used to fit the experimental Tg data in series B3 through B6, are listed under the corresponding curves in Figure 1.

Generally q increases as the concentration of interactive groups increases. The exception appears to be series B6 where the Tg's and the compositions of the component copolymers are the most closely matched. When k=1, q reflects the extent of destabilization of the backbone (15).

Conclusions

Phase behavior of blends with equivalent moles of DNBM and Nvc, R=1, are compiled in Figure 2. Transition temperatures are plotted against the average concentration of interactive groups, referred to as the average perturbation. From this

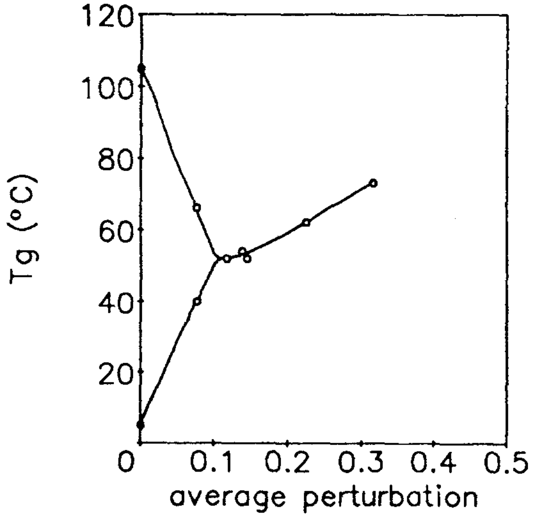


Figure 2 Glass transition temperatures of the six blends in which R=1, plotted as a function of average perturbation

figure it is evident that compatibilization occurs somewhere below 12 mole% interactive groups.

Concentrations of interactive groups required to achieve compatibility through charge transfer interactions are lower for this system than for the other charge transfer systems reported in the literature. Since polymer compatibility is facilitated by low molecular weight of the components (17), the very low molecular weight of the acceptor copolymers is a plausible reason for the low concentration of charge transfer groups required for compatibilization of polystyrene and poly(methyl acrylate).

Acknowledgements

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